

# **Soluble polythiophenes as anticorrosive additives for marine epoxy paints**

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## Abstract

This study compares the resistance against corrosion of a marine epoxy primer modified with  $\text{Zn}_3(\text{PO}_4)_2$  (10 wt. %) or a small concentration (0.3 wt. %) of conducting polymer as inorganic or organic anticorrosive pigment, respectively. More specifically, the behavior of three different conducting polymers has been evaluated: polyaniline emeraldine base, poly(3-thiophen-3-yl-acrylic acid methyl ester) and poly(2-thiophen-3-yl-malonic acid dimethyl ester), the latter two being soluble polythiophene derivatives bearing carboxylate side groups. In a first stage, the structural, thermal and mechanical properties of all the modified epoxy coatings were characterized using infrared spectroscopy, thermogravimetric analyses and stress-strain assays, respectively. After this, accelerated corrosion assays have evidenced that the degree of protection imparted by a small concentration of polyaniline is higher than that obtained using 10 wt. % of  $\text{Zn}_3(\text{PO}_4)_2$ . Indeed, polyaniline has been found to be more effective as anticorrosive additive than the two polythiophene derivatives. This fact has been attributed to the electroactivity of the former, which is higher than that of the latter. Thus, the ability to store charge has been proposed to be also responsible of protection against corrosion imparted by organic additives, based on conducting polymers.

*Keywords:* conducting polymer, epoxy resin, anticorrosive paints, mechanical properties, thermal stability.

## 1. Introduction

Marine corrosion is a topic of great interest based in the electrochemical reaction of steel, active metals and alloys with oxygen in presence of sea water. This type of corrosion depends on the particular conditions of the medium, as temperature, oxygen and salts concentration, and presence of marine organisms, which lead to the well-known bio-fouling phenomenon. Although some ionic compounds are protective in form of calcareous deposits, particularly in immersed structures, the presence of chloride ions inside the sea water and in marine environments is the origin of marine corrosion, giving place to both generalized and pitting corrosion in metallic structures [1].

Organic coatings and, in particular, paints became an important solution to mitigate the consequences of corrosion during the second half of 20<sup>th</sup> century. Thermoplastic and thermosetting polymers have been successfully applied in different systems as both anticorrosive paints and powder coatings for several applications [2,3]. In all cases, the main function of such protective coatings is to avoid the access of pollutants to the surface, being also an important dielectric barrier between the metallic substrate and the environment [4].

In spite of the prolific characteristics of paints in terms of both composition and applications, alkyd and epoxy resins have been considered for years as the most important primers in the market [5]. These conventional anticorrosive primers usually contain inhibitors based on hexavalent chromium, lead compounds and zinc phosphate derivatives [6-8], the latter being the most widespread at present time due to its ability for steel passivation in acidic media [7-9]. Although zinc phosphate derivatives provide good results, in some cases their anticorrosive performance is lower than that of chromates [10]. On the other hand, in recent years we reported that conducting polymers (CPs) can be successfully used as anticorrosive additives to modify the formulation of conventional organic coatings [11], the most important benefit of this technology being that a very low concentration of CP is needed. Interestingly,

we found that, in principle, the chemical nature of the anticorrosive additive can extend from polythiophene (PTh) [12-16] or polypyrrole (PPy) [13,16,17] derivatives to polyaniline (PAni) [17-19], even though the corrosion protection imparted by each CP may be limited by its compatibility with the paint formulation (*i.e.* the achievement of good and homogeneous dispersions on the resin formulation is essential). Many efforts have been focused on solve the high insolubility of CPs in coatings formulations, in order to improve the dispersion and efficiency of CPs as anticorrosive additive. As an example, Gergely *et. al.* have recently studied the corrosion protection of zinc-rich epoxy paint coatings with highly dispersed polypyrrole-deposited alumina monohydrate particles [20-22], achieving a well-balanced active/passive function in the hybrid coating containing zinc and PPy. Hou *et. al.* studied the incorporation of different size of polyaniline nanoparticles to an epoxy paint, obtaining good results with nanoparticles doped with  $\text{FeCl}_2$  [23]. They concluded that PAni also play a rule in the barrier protection if the particle size is suitable to provide a good dispersion inside the coating.

In a recent study we investigated the efficacy of the conducting emeraldine salt form of PAni (PAni-ES) as anticorrosive additive for an epoxy paint based on diglycidyl ether of bisphenol A and polyamide [17]. The concentration of the CP in the paint formulation was varied from 0.3 to 1.5 wt.%. Interestingly, accelerated corrosion assays showed that the addition of PAni-ES improves the resistance of the paint, the highest inhibition of corrosion being obtained for the lowest CP concentration (*i.e.* 0.3 wt. %). Furthermore, this CP polymer was found to act as adhesion promoter, this behavior being fully consistent with that found for PAni coatings [24-27].

More recently, an alkyd formulation containing zinc phosphate (10 wt.%) was prepared and subsequently modified replacing the latter anticorrosive additive by a very low concentration of CP [28]. Specifically, three modified paints were formulated, which

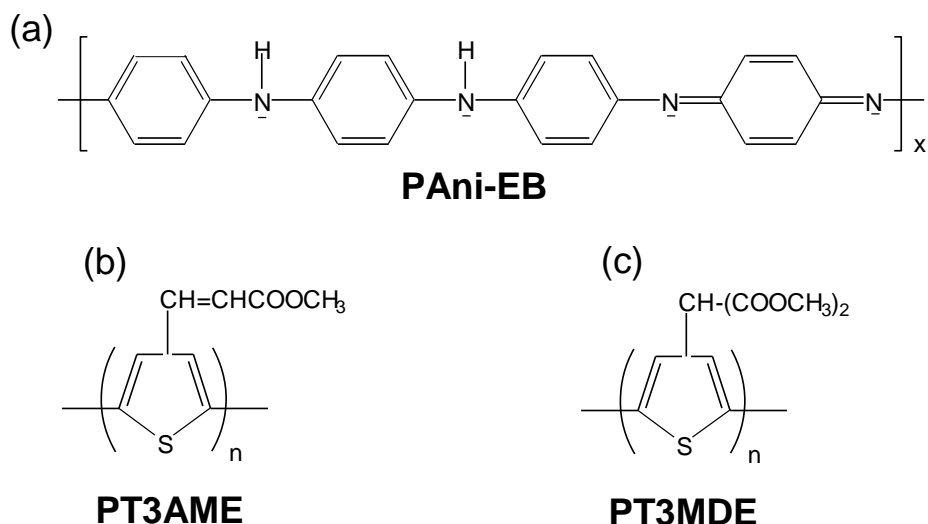
contained polyaniline emeraldine base (PAni-EB), PAni-ES and a partially oxidized PTh derivative. The properties and corrosion resistance of the four alkyd coatings were characterized. Among the three modified paints, the one containing PTh showed the best adherence and the highest corrosion resistance. This was attributed to the fact that the miscibility of the PTh derivative with the alkyd formulation is better than that of PAni. Furthermore, accelerated corrosion assays revealed that the corrosion resistance of the paint with PTh is several orders of magnitude higher than that with zinc phosphate. The PTh derivative was found to induce the formation of a passivating and well-adhered layer between the coating and the surface, preventing the access of chloride anions and oxygen to the substrate.

As a continuation of our recent study on alkyd primers [28], in this work we compare the performance as anticorrosive pigments of three CPs and zinc phosphate when they are used in a commercial epoxy primer recommended for the protection of steels surfaces in contact with marine environments. Specifically, very small weight percentages of two recently described PTh derivatives [29,30], which show good solubility in organic solvents, and PAni-EB have been employed. The two main objectives of this study are: *(i)* to examine the performance as corrosion inhibitors of these two PTh derivatives, comparing them with zinc phosphate, a conventional inorganic pigment; and *(ii)* to compare the efficacy as anticorrosive additive of the two soluble PTh derivatives with that of the less soluble PAni-EB when used in epoxy primers. Accordingly, our final aim is to find a soluble CP for the satisfactory substitution of classical zinc-containing corrosion inhibitors used in marine epoxy primers, as we recently did for industrial alkyd primers [28].

## **2. Methods**

*2.1. Materials.* The epoxy primer used in this work was kindly supplied by Pinturas Hempel S.A. This primer was prepared by mixing a stoichiometric amount of Epikote 3011 (Hexion) and Crayamid 115 (Cray Valley), a mixture of inert pigments (PVC= 27%), and a mixture of alcoholic solvents and aromatic hydrocarbons (15% w/w). This composition was free of anticorrosive pigments and additives.

The chemical formulas of the three CPs used in this work, PANi-EB, poly(3-thiophen-3-yl-acrylic acid methyl ester) (PT3AME) and poly(2-thiophen-3-yl-malonic acid dimethyl ester) (PT3MDE), are displayed in Scheme 1. PANi-EB is the undoped form of PANi (Scheme 1a). PT3AME is a PTh derivative with a conjugated substituent in which the polymer backbone and the electron-withdrawing carboxylate group are separated by a double bond (Scheme 1b) [29]. Thus, the aim of the acrylate substituent in PT3AME is not only to improve the solubility and dispersion of the PTh chains but also to enlarge the conjugated system from the backbone to the side chain, which results in an improvement of the electronic properties with respect to unsubstituted PTh [29]. PT3MDE is a PTh derivative bearing a substituent with two carboxylate groups per structural unit (Scheme 1c) [30]. This CP is soluble in a number of solvents such as chloroform, tetrahydrofuran, dimethyl sulfoxide, acetone and dichloroacetic acid. PANi-EB was purchase from Aldrich (catalog number: 476706) whereas both PT3AME and PT3MDE were synthetized in our laboratory by chemical oxidative coupling polymerization using the experimental procedures recently described [29,30]. Zinc phosphate,  $Zn_3(PO_4)_2$ , an inorganic additive commonly used with both aqueous and organic primers, was purchased from Europigments S.A.



Scheme 1

Corrosion experiments were performed using a naval steel (St F111) as metallic substrate. The elemental composition of this steel is: C = 0.20%, Mn= 1.40%, S = 0.045%, and N= 0.009%, the density being  $7.90 \times 10^3 \text{ kg/m}^3$ . Rectangular test pieces of  $40 \times 50 \times 1 \text{ mm}^3$  with a diameter hole of 6.5 mm were previously degreased with acetone and stored in dried atmosphere until the coating application, using calcium chloride as dryer in a recipient connected to the vacuum.

*2.2. Preparation and application of the paints.* The epoxy paints without corrosion inhibitor and with  $\text{Zn}_3(\text{PO}_4)_2$  (10 wt.%), PT3AME (0.3 wt.%), PT3MDE (0.3 wt.%) and PAni-EB (0.3 wt.%) have been denoted EP-0, EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10, EP/PT3AME-0.3, EP/PT3MDE-0.3 and EP/PAniEB-0.3, respectively. Paints were applied by immersion (one coat) of the metallic substrate in a base/solvent/hardener composition with the mixing ratio recommended by the manufacturer. These compositions are detailed in Table 1. In the case of EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10, small quantities of BYK 500 (0.0809 g) and BYK 525 (0.0457 g), from BYK Chemie, were required to aid the pigment dispersion. Initially, PAni-EB was dissolved in a small volume of xylene (3-5 mL) while both PT3AME and PT3MDE were dissolved in

trichloromethane (3-5 mL), before the addition to the paint formulation. It should be remarked that a good dispersion of the CP is necessary to allow a suitable application of the paint on the metallic substrate and to obtain a covering power able to guarantee the desired protective characteristics. The thickness of the films obtained using this procedure was determined for 10 samples of each class using a machine model Uno-Check Fe from Neurtek S.A, the resulting average thickness values being displayed in Table 1.

*2.3. Characterization.* A Jasco 4100 FTIR spectrophotometer with a resolution of  $4\text{ cm}^{-1}$  in the absorbance mode was used for the structural characterization of the coatings. Samples were placed in an attenuated total reflection accessory with thermal control and a diamond crystal (Mk II Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma). Thermogravimetric analyses were carried out with a Perkin-Elmer thermogravimetric analyzer TGA-6 at a heating rate of  $10^{\circ}\text{C}/\text{min}$  under nitrogen atmosphere and a temperature range from 30 to  $850^{\circ}\text{C}$ . The mechanical properties of the paints were evaluated through stress-strain assays with a Zwick Z2.5/TN1S testing machine. Regular films were prepared by evaporation of the volatile organic solvent of the paint formulation at room temperature. Plate samples with a length of 30 mm, a width of 3 mm and thickness varying from 200 to 300  $\mu\text{m}$ , measured with Uno-Check FE machine, were cut out from the films and used for the assays. The deformation rate was 10 mm/min. Mechanical parameters (*i.e.* Young's modulus, the tensile strength and the elongation at break) for each coating were averaged considering 10 independent measurements.

*2.4. Corrosion assays.* Corrosion tests were performed using a home-made equipment developed in our laboratory [31]. This device was designed to perform accelerated immersion assays in an aggressive solution medium through controlled cycles. The solution medium consists of an aqueous solution of NaCl (3.5 wt.%, pH=6.6) stored in a polypropylene



container. The operating conditions programmed for each cycle were: (i) immersion of coated steel sheets (15 min); (ii) wring out (30 min); (iii) drying stage with bulbs (230V-100W, 10 min, ~40 °C); and (iv) cooling time at room temperature (5 min). Painted panels were sealed on the edges and around the hole used for securing the pieces. The samples were tested in the solution medium during 30 days (*i.e.* 720 cycles). Laboratory conditions were 20 °C and relative humidity of 50%. After the beginning of the test, the samples were removed at 120, 240, 480 and 720 hours. The corrosion of steel was monitored by visual and microscopy inspections, as described on the standard method ASTM D-1654.

Scanning electron microscopy (SEM) studies of the coating surfaces were performed using a Focussed Ion Beam Zeiss Neon 40 scanning electron microscope, equipped with an EDS system. Photographs and micrographs of the samples were taken before exposure to the aggressive solution.

### **3. Results and Discussion**

#### *3.1. Characterization of the coatings*

The structural, thermal and mechanical characterization of EP-0 was described in a previous work [17]. Accordingly, in this section we focused in the formulations modified by the addition of  $\text{Zn}_3(\text{PO}_4)_2$ , PT3AME, PT3MDE and PAni-EB to the epoxy paint. Figure 1 compares the absorption spectrum of EP-0 with those of the four modified formulations. It is worth noting that the addition of the inorganic and organic corrosion inhibitors does not produce any structural change, the absorption bands remaining practically unaltered. No absorption band is detected at  $917\text{ cm}^{-1}$ , which is consistent with the absence of terminal epoxy groups and corroborates with the fact that coatings are completely cured. The presence of strong bands in the  $1249\text{-}1041\text{ cm}^{-1}$  region has been identified as  $\text{C}(\text{Ar})\text{-O-C}(\text{alkyl})$  ether group of bisphenol A, a thermoplastic polymer typically found in epoxy resins and

characterized in previous works [12,32]. Furthermore, the presence of aromatic C(Ar)–C has been determined through the characteristic stretching absorption bands at around 1508 and 1608  $\text{cm}^{-1}$ . Another interesting band corresponds to the broad and strong absorption at 1100-900  $\text{cm}^{-1}$ , which reveals the presence of silicates (O-S-O) and phosphates (O-P-O) groups. The former is frequently employed in paint formulations as inert additives to improve the rheological properties of the emulsion and the latter was employed as anticorrosive additive in the case of paint EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10. Both polar groups, silicates and phosphates, have absorption bands in the same position due to the similarity of bond stretching or vibration mode in the IR fingerprint region.

The thermal stability of the five coatings was studied by thermogravimetry, the resulting curves being compared in Figure 2. The thermal behavior is not influenced by the addition of corrosion inhibitors. Thus, all the paints undergo a weight loss of 10-15% when the temperature increases from 60 to 330°C, which has been attributed to the evaporation of solvents trapped in crosslinked polymer chains as well as to the decomposition of low-molecular weight polymer fractions. With increase temperature, the weight loss increases, reaching values of 45-50% at 500°C. This pronounced fall corresponds to the degradation of the cured epoxy resin. Finally, the degradation of some inorganic components is observed at higher temperatures. The latter process is particularly relevant for the EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10 paint, which shows a curve with a pronounced and progressive fall among 500-850°C. Moreover, the profile obtained for the EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10 paint shows a discontinuity between 500-550°C with a weight loss of about 10-12%, which corresponds to the decomposition of the zinc phosphate inorganic additive. The percentage of inorganic pigments and/or additives contained in the paints is reflected by the char-yielded at 850°C: 45%, 23%, 40%, 39% and 39% for EP-0, EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10, EP/PT3AME-0.3, EP/PT3MDE-0.3 and EP/PAniEB-0.3, respectively. On the other hand, Figure 2 evidences that the thermal stability of EP-0

decreases upon the addition of corrosion inhibitors (*i.e.* modified paints starts the decomposition of the resin at a lower temperature). This effect is very similar for all the corrosion inhibitors, which allows us to conclude that the thermal stabilities of the epoxy paints modified with CPs and with  $\text{Zn}_3(\text{PO}_4)_2$  are practically identical.

The mechanical properties of the epoxy coatings studied in this work are listed in Table 2 whereas the strain-stress curves are displayed in Figure 3. As it can be seen, all the paints are brittle materials with moderate Young's modulus ( $E$ ) and low elongation at break ( $\epsilon_b$ ). The Young's modulus varied between 462 (EP/PT3MDE-0.3) and 1562 MPa (EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10) while the tensile strengths ( $\sigma_{\max}$ ) ranged from 17 (EP/PT3MDE-0.3) to 37 MPa (EP-0). Although the elongation at break of EP-0 ( $\epsilon_b = 6.2\%$ ) improves considerably upon the addition of a small concentration of PT3MDE ( $\epsilon_b = 8.7\%$ ) and, especially, PT3AME ( $\epsilon_b = 10.0\%$ ), the Young's modulus and the tensile strength deteriorate. The presence of  $\text{Zn}_3(\text{PO}_4)_2$  in the epoxy composition provokes a very significant reduction of both the elongation at break ( $\epsilon_b = 2.9\%$ ) and the tensile strength ( $\sigma_{\max} = 20$  MPa). On the other hand, the Young's moduli increases ( $E = 1562$  MPa) and provokes the formation of a very brittle epoxy film. Despite of these limitations, it should be remarked that the mechanical properties listed in Table 2 are very similar to those reported for commercial paints that are typically used for corrosion protection in marine environments [12,17,19]. On the other hand, Figure 3 shows that the EP-0 formulation presents both plastic and elastic limits. The addition of  $\text{Zn}_3(\text{PO}_4)_2$ , PT3AME and PT3MDE preserves this behavior while the formulation with PANi-EB only presents elastic limit. The latter feature has been attributed to the existence of secondary reactions between the amine groups of PANi and some components of the epoxy formulation.

### *3.2. Accelerated corrosion assays*

Samples coated with the EP-0 epoxy paint and its four modified formulations are displayed in Figure 4. All photographs are related to the panels after to rinse with water at a temperature up to 45°C and before to scrape the specimens in order to evaluate the blistering formation around scribe and rust. In the EP-0 samples, the apparition of areas with blisters and rust under the film were detected after only 240 cycles. The resistance against corrosion of this epoxy coating improves upon the addition of  $\text{Zn}_3(\text{PO}_4)_2$ , as expected. Thus, the degree of blistering and rusting after 240 cycles were smaller for EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10 than for EP-0. The CP-containing formulations, especially the EP/PAniEB-0.3, showed the higher anticorrosive properties. Thus, the blistering formation after 720 cycles is practically inappreciable for EP/PAniEB-0.3 while it is smaller for EP/PT3AME-0.3 and EP/PT3MDE-0.3 than for EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10. On the other hand, we observed that the color of panels painted with EP/PT3AME-0.3 and EP/PT3MDE-0.3 changed with the time of exposure to the corrosive environment, which has been attributed to the variation of the  $\text{FeCl}_3$  content into the paints and, probably, to the oxidation process suffered by CP after chlorine permeability to the film. EP/PAniEB-0.3 showed better color stability during corrosion assays.

Figure 5 represent the progression of rust from scribe against time according to the ASTM standard method D-1654. The progress of rust indicates the loss of adherence near to the scribe mark. After 720 cycles, the sample coated with the EP-0 formulation presented 25 mm of rust compared to the 5 mm of EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10 and EP/PAniEB-0.3, evidencing that water, oxygen and chloride ions cannot overcome the protective barriers promoted by  $\text{Zn}_3(\text{PO}_4)_2$  and PAni-EB corrosion inhibitors. The addition of PT3AME and PT3MDE enhances the corrosion protection with respect to the unmodified epoxy formulation, presenting 17 and 8 mm of rust, respectively. Although PT3AME and PT3MDE improve significantly the anticorrosive properties of EP-0, the protection imparted by these two polythiophene derivatives is lower than those obtained with  $\text{Zn}_3(\text{PO}_4)_2$  and PAni-EB. Moreover, this

behavior is practically independent of the number of cycles. These results are in agreement with our previous studies [17], which indicated that PAni-EB promotes significantly the adherence between the coating and the steel. In opposition, in our recent study with alkyd compositions [28], the protection performance provided by the PTh ester derivative was found to be better than that of PAni-EB. Probably, the electroactivity, i.e. the CP capability to experience several oxidation-reduction cycles, for this kind of PTh derivative is better than that supported by PAni-EB, therefore the CP can be continuously re-charged by re-oxidation and discharged by reduction processes. This protection mechanism would be in accordance with the mechanism proposed by A. Michalik and M. Rohwerder [33]. Nevertheless, the anticorrosive behavior of CPs depends on the nature of the polymer resin. In the present study, the adherence of coatings was only qualitatively investigated, *i.e.* with visual inspection after removing the film from the scribe mark, according to the ASTM 1654, and the resultant observation are displayed on Table 1. Figure 6 shows the panels that were scrapped after 120, 240, 480 and 720 cycles of accelerated corrosion assays.

SEM micrographs of the coatings surfaces, which are displayed in Figure 7, allowed us to reach some conclusions regarding the variability of organic-inorganic anticorrosive protection found in this work. Films without  $\text{Zn}_3(\text{PO}_4)_2$  or CPs show higher particles agglomerates at surface (Figure 7a) and, at higher magnification scale (Figure 7b), seems more porous than those with such additives. This supports the behavior of EP-0, which was worse than those films with anticorrosive additives (*i.e.* the water uptake should be very fast through coating. On the other hand, micrographs of the surfaces of coatings with  $\text{Zn}_3(\text{PO}_4)_2$  and CPs reveals the presence of an amount of poorly dispersed pigments and additives, as is evidenced by the white particles in the Figures 7c-7d (EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10), 7e-7f (EP/PAniEB-0.3) and 7g-7h (EP/PT3AME-0.3). Interestingly, the PT3AME-containing coating shows many spherical holes at surface compared to the EP/PAniEB-0.3coating. However, these concave shapes are just

surface defects that appeared after solvent evaporation. Due to its high solubility, the small CP particles, weakly adhered to the epoxy matrix, can be easily detached when a high vacuum system, like that of the sample chamber in the SEM microscope, is applied. This kind of concave forms were also observed for the poly[2,2'-(3-methylacetate)thiophene], as was reported in previous works [28,34]. SEM micrographs of EP/PT3MDE-0.3 are not showed because they were very similar to those of EP/PT3AME-0.3.

Micrographs of EP/PAni-EB-0.3 (Figure 7f) show a smooth surface with few white particles inside the epoxy film, which is consistent to a good dispersion of PAni-EB compared to  $\text{Zn}_3(\text{PO}_4)_2$ . Figure 7h also shows a smooth surface but corrosion results were not the desirable due to different factors, like the high hydrophilicity and, especially, the low electroactivity of the CPs bearing ester groups (see below).

Summarizing, results reported in Figures 4-7 show that PAni-EB performs better corrosion protection than PT3AME, PT3MDE and  $\text{Zn}_3(\text{PO}_4)_2$  when used as anticorrosive additive of epoxy coatings. It is worth noting that undoped PAni-EB was reported to be more effective as anticorrosive additive than the doped PAni-ES [35,36], even though it is generally accepted that the ability of CPs to intercept electrons at the metal surface and to transport them in a very effective mechanism to retard corrosion. However, in a recent study we demonstrated that the ability to store charge (*i.e.* the electroactivity) is also responsible of protection against corrosion [15,16]. More specifically, we found that the mechanism based on the ability of organic materials to act as molecular condensers predominate over the mechanism based on the electrical properties. The results obtained in the present work are fully consistent with the previous observation since PAni-EB shows higher ability to store charge but lower electrical conductivity than the PTh derivatives. Thus, the success of PAni-EB as anticorrosive additive should be attributed to the fact that the epoxy formulation used in this work does not alter its intrinsically high redox capacity (*i.e.* ability to oxidize and reduce

in a reversible way) [37,38]. In contrast, the electroactivity of PT3MDE and, especially, PT3AME is very low because of the intrinsic tendency of PTh and its derivatives to promote crosslinking [29,30]. Accordingly, the protection imparted by EP/PT3MDE-0.3 and EP/PT3AME-0.3 is essentially based on their ability to transport charge, which was found to be only moderate. More specifically, the electrical conductivity of PT3MDE and PT3AME was reported to be 6 S/cm [30] and 15 S/cm [29], respectively, these values being significantly lower than those reported for other PTh derivatives [e.g. 315 S/cm for poly(3,4-ethylenedioxythiophene)] [39]. Thus, soluble CPs able to provide good miscibility with the epoxy resin are not enough to produce effective organic anticorrosive additives, fulfillment of other requirements like intrinsically high electroactivity and/or electrical conductivity being necessary. On the other hand, it is worth noting that PAni-EB has many amine groups that are capable of complexing metal ions. In an early study, it was reported that a PAni-EB film led to the extraction of Cu from the top several hundred angstroms of Al 2024-T3 [39], thus removing the Cu/Al galvanic couple that is primarily responsible for the corrosion behavior of this alloy. These complexing abilities of PAni-EB may also play a role in this process.

#### **4. Conclusions**

A marine epoxy paint has been modified by adding a 10 wt. % of  $\text{Zn}_3(\text{PO}_4)_2$  or a very low concentration of conducting polymer (PT3AME, PT3MDE or PAni-EB) as anticorrosive pigment. FTIR spectroscopy studies showed that the structure of the four modified formulations is practically identical to that of unmodified one, epoxy resin being completely cured in all cases. Thermogravimetric analyses indicated the thermal stability of the epoxy primer decreases upon the addition of both organic and inorganic corrosion inhibitors. On the other hand, films prepared using the unmodified epoxy primer and the formulations

containing  $\text{Zn}_3(\text{PO}_4)_2$ , PT3AME and PT3MDE presented both plastic and elastic yield, whereas the no plastic behavior was found for the formulation with PANi-EB.

As it was expected, the resistance against corrosion of the epoxy primer improved upon the addition of an anticorrosive pigment. The highest corrosion protection was provided by the formulation with 0.3 wt. % of PANi-EB. Although PT3AME and PT3MDE enhanced the corrosion protection imparted by the unmodified epoxy paint, the electroactivity and electrical conductivity of these polythiophene derivatives was not large enough to improve the outcomes obtained with the PANi-EB-containing paint. The overall of the results obtained in this work allows us to conclude that, although the miscibility between the different components is essential to obtain a good paint, CPs used as corrosion inhibitors must satisfy other requirements, such as high electroactivity and/or electrical conductivity.

## Acknowledgements

This work has been supported by MICINN and FEDER funds (MAT2009-09138 and MAT2012-34498) and by the DIUE of the Generalitat de Catalunya (contract number 2009SGR925). Support for the research of C.A. was received through the prize “ICREA Academia” for excellence in research funded by the Generalitat de Catalunya.

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## Captions to Figures

**Figure 1.** Infrared absorption spectra of the epoxy formulations studied in this work: EP-0, EP/Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-10, EP/PT3AME-0.3, EP/PT3MDE-0.3 and EP/PAniEB-0.3.

**Figure 2.** Thermogravimetric curves of the epoxy paints studied in this work: EP-0, EP/Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-10, EP/PT3AME-0.3, EP/PT3MDE-0.3 and EP/PAniEB-1. Scan rate: 10°C/min.

**Figure 3.** Tensile strain-stress curves for the epoxy paints studied in this work: EP-0, EP/Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-10, EP/PT3AME-0.3, EP/PT3MDE-0.3 and EP/PAniEB-0.3. Deformation rate: 10 mm/min.

**Figure 4.** Test panels of the epoxy coating without anticorrosive pigment (EP-0) and modified with Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (10 wt.%), PAni-EB (0.3 wt.%), PT3AME (0.3 wt.%) and PT3MDE (0.3 wt.%) before (0h) and after accelerated corrosion cycles (120, 240, 480, 720h). The length scale is indicated at the bottom.

**Figure 5.** Progression of rust from scribe against the number of accelerated corrosion cycles according to ASTM standard method D-1654 for the epoxy paints studied in this work: EP-0, EP/Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-10, EP/PT3AME-0.3, EP/PT3MDE-0.3 and EP/PAniEB-0.3.

**Figure 6.** Scrapped test panels of the epoxy coating without anticorrosive pigment (EP-0) and modified with Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (10 wt.%), PAni-EB (1.0 wt.%), PT3AME (0.3 wt.%) and PT3MDE (0.3 wt.%) after 120, 240, 480 and 720 accelerated corrosion cycles.

**Figure 7.** SEM micrographs of the surface of films studied in this work before the immersion of the coated panels in the aggressive solution. Scale bar: 20 µm (left) and 1 µm (right).

**Table 1.** Composition (in grams) of the epoxy formulations used in this work, thickness of the films after drying obtained by immersion of the steel substrate in the composition (one coat), and adherence of the film to the substrate.

<i>Paint</i>	<i>Base</i>	<i>Hardener</i>	<i>Corrosion inhibitor</i>	<i>Xylene</i>	<i>Thickness (<math>\mu\text{m}</math>)</i>	<i>Adherence<sup>a</sup></i>
EP-0	41.37	8.62	-	12.50	138	++
EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10	74.79	15.32	10.09	16.13	113	++++
EP/PT3AME-0.3	81.53	18.64	0.30	10.36	123	++
EP/PT3MDE-0.3	81.53	18.64	0.30	10.36	128	+++
EP/PAniEB-0.3	82.47	17.17	0.30	10.63	125	++++

<sup>a</sup> The code used to indicate the qualitative adherence is: +: bad, ++: medium; +++: good; ++++: excellent.

**Table 2.** Mechanical properties of the epoxy paints studied in this work.

	<b>E (MPa)<sup>a</sup></b>	<b><math>\sigma_{\max}</math> (MPa)<sup>b</sup></b>	<b><math>\epsilon_b</math> (%)<sup>c</sup></b>
EP-0	896	37	6.2
EP/Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> -10	1562	20	2.9
EP/PT3AME-0.3	675	19	10.0
EP/PT3MDE-0.3	462	17	8.7
EP/PAniEB-0.3	1063	19	7.4

<sup>a</sup> Young's modulus. <sup>b</sup> Tensile strength. <sup>c</sup> Elongation at break.

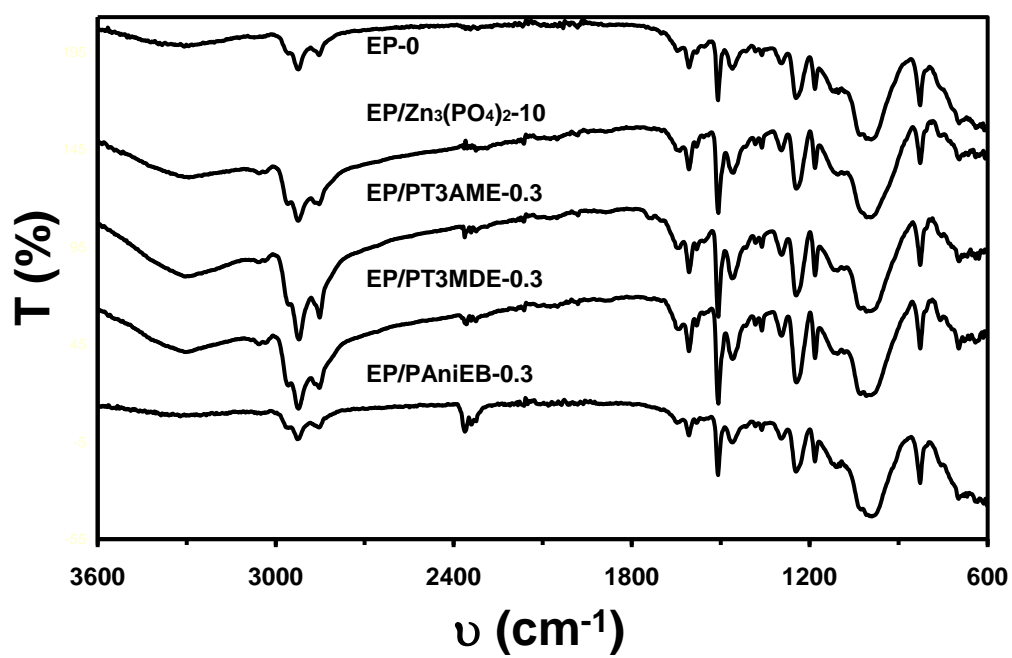


Figure 1

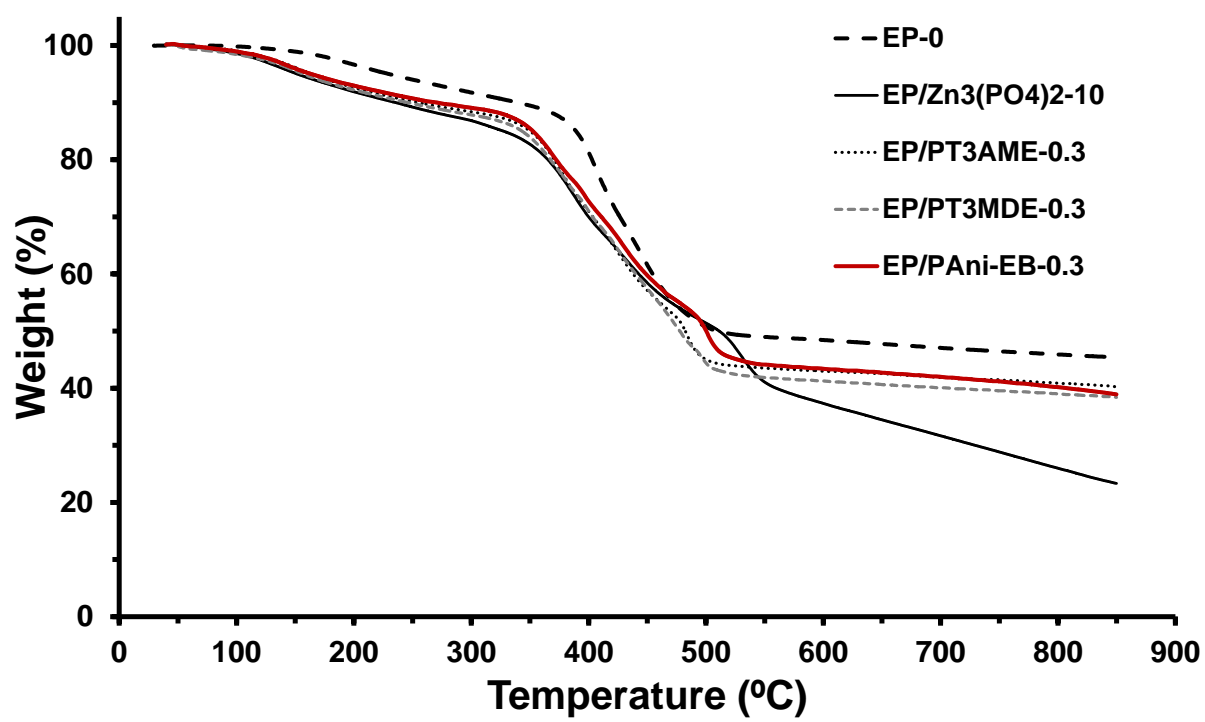


Figure 2



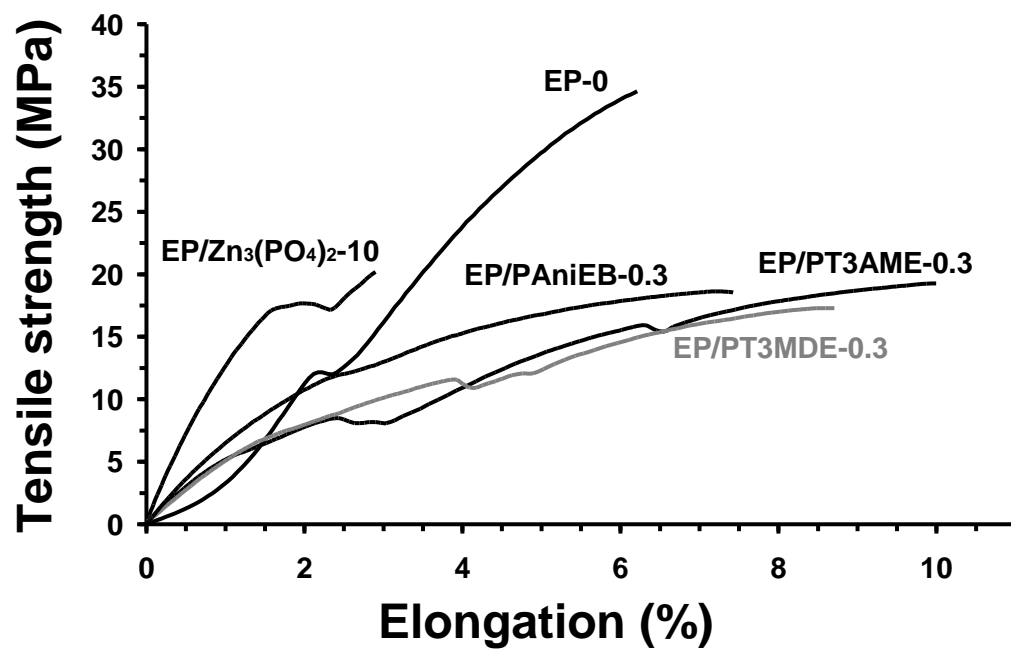


Figure 3

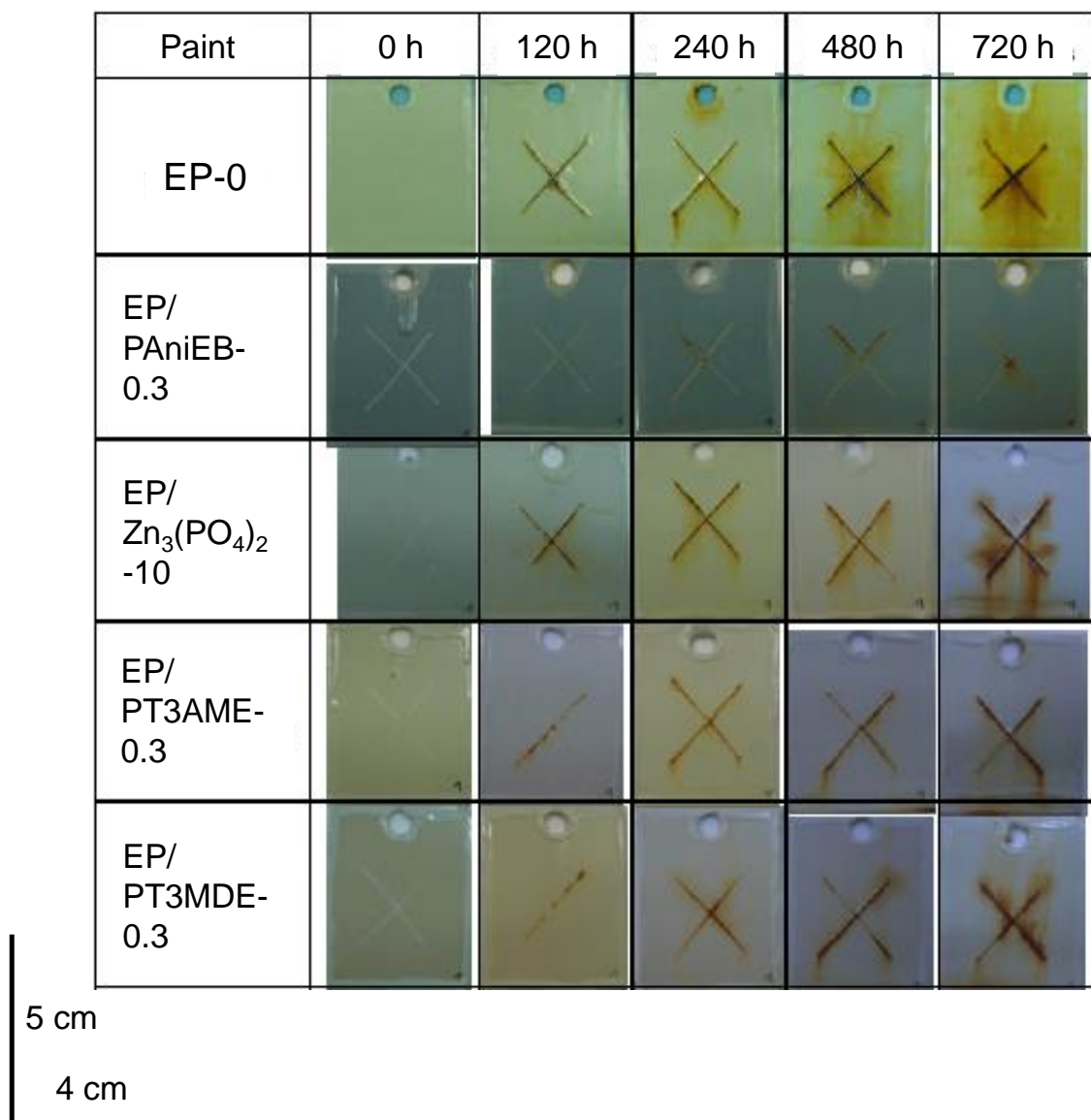


Figure 4

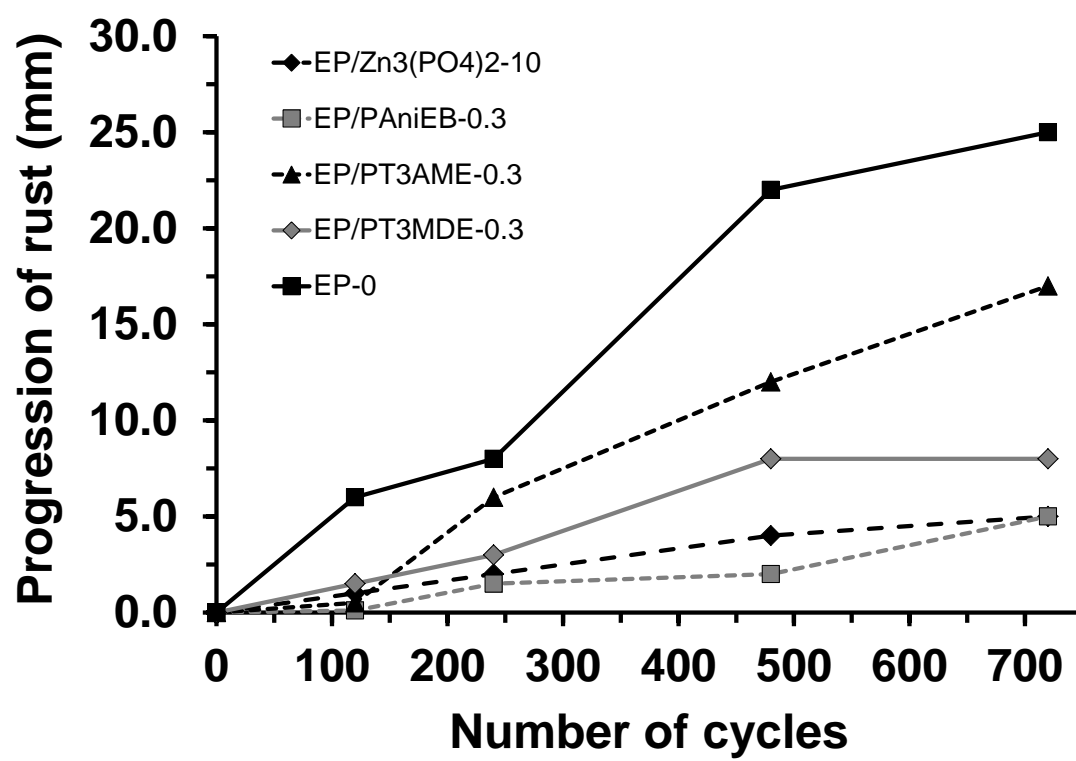


Figure 5















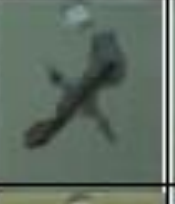





Paint	120 h	240 h	480 h	720 h
EP-0				
EP/ PAniEB-0.3				
EP/ $\text{Zn}_3(\text{PO}_4)_2$ -10				
EP/ PT3AME-0.3				
EP/ PT3MDE-0.3				

Figure 6

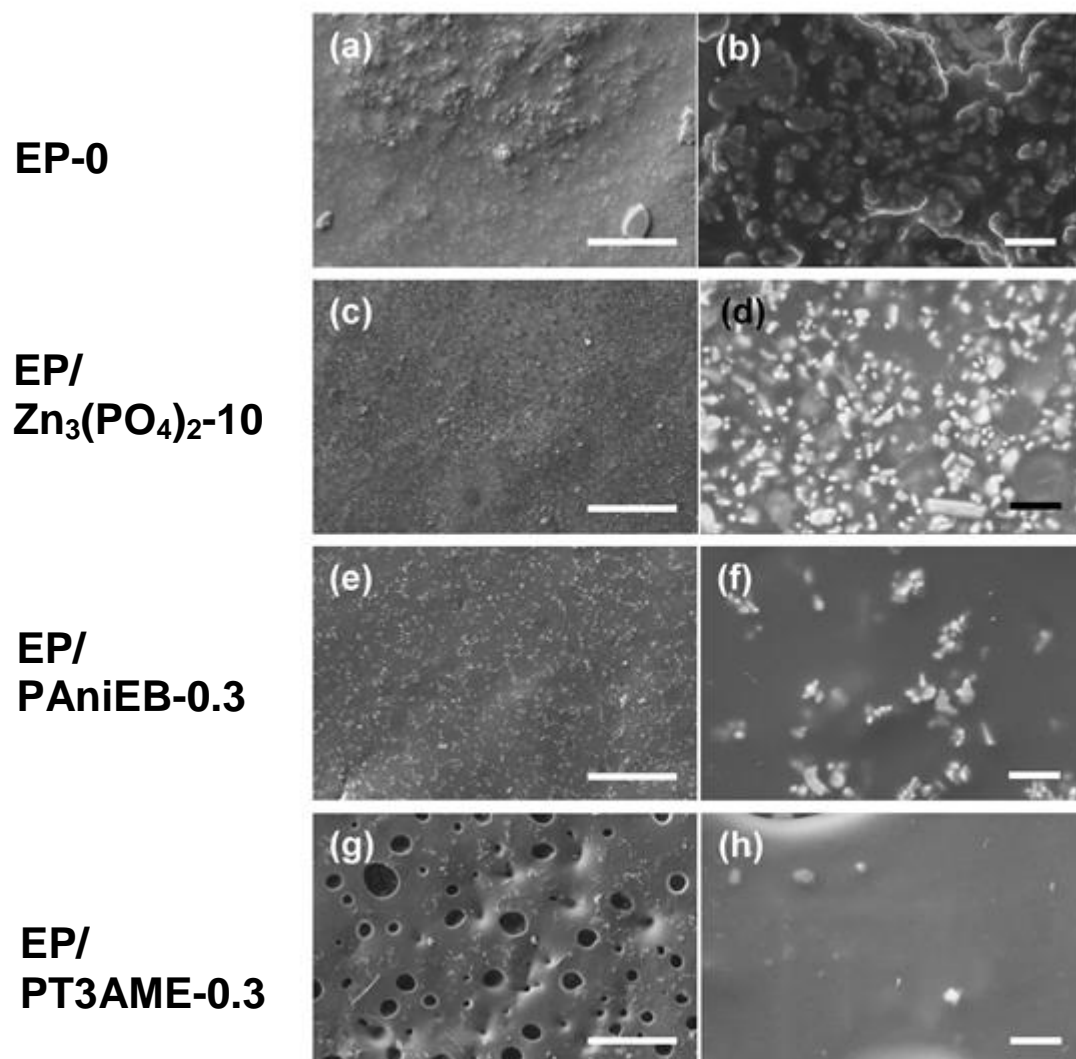


Figure 7